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Procedia Earth and Planetary Science 13 (2015) 312 – 315

Procedia
Earth and Planetary Science

11th Applied Isotope Geochemistry Conference, AIG-11 BRGM

Evidence for nutrient biolifting in Hawaiian climosequence soils as revealed by alkaline earth metal stable isotope systematics

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Abstract

Plants are known to scavenge nutrients such as phosphorus (P) from rock subtrates and concentrate those nutrients at the surface in order to satisfy long-term nutritional requirements. Using the stable isotope systematics of calcium (Ca), strontium (Sr) and barium (Ba) as proxy tracers, here we test the hypothesis that soils along a Hawaiian climosequence have "biolifted" P and other nutrients such as Ca from depth and concentrated those nutrients at the surface. Relative to isotope compositions in the volcanic soil parent materials, exchangeable Ca, Sr and Ba in the shallowest soils at sites having evidence for P biolifting are light confirming the role for plant uptake of these elements while exchangeable Ca, Sr and Ba of deeper soils at those sites are similar or heavy suggesting a complementary pool. In this pedogenic system Ca and Sr are more susceptible to leaching than Ba, thus Ba isotopes provide the most resilient evidence for biolifting across the climate gradient and a useful proxy for P biodynamics.

Peer-review under responsibility of the scientific committee of AIG-11

Keywords: metal stable isotopes; biolifting; alkaline earth elements; pedogenesis; cation exchange pool

1. Introduction

"Biolifting", a conceptual framework that links inorganic nutrient uptake by plants to rock weathering, is characterized by depletion of a nutrient in deeper soils as a result of chemical weathering and enrichment of that nutrient in shallow soils using of the plant root network as the uptake pathway[1]. Demonstration of biolifting can be

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Peer-review under responsibility of the scientific committee of AIG-11
doi:10.1016/j.proeps.2015.07.074

complicated in that other processes such as aerosol and dust deposition can lead to enrichment of inorganic nutrients at the surface[2]. Distinguishing between these two (and other) processes may be possible by identifying differences in isotope composition between biolifted vs. atmospherically-deposited nutrients. While the isotope approach is useful for nutrients such as calcium (Ca) that have either multiple stable isotopes[3] or a radiogenic isotope[4], it is not possible for mono-isotopic nutrients such a P and thus the use of proxy isotope tracers is required. Here we develop a multi-stable isotope approach to support our working hypothesis that biolifting of P has occurred along a climosequence developed on volcanic rocks on the Big Island of Hawaii[5]. We propose that similarities in depletion and enrichment of the alkaline earth elements Ca, strontium (Sr) and barium (Ba) to those of P in soils having evidence of P biolifting suggests that their stable isotopes provide a useful proxy for P biodynamics. Previous studies have shown that plants preferentially take up light Ca, Sr and Ba from soils[3,6,7] and thus isotope compositions in surface soils that are lighter than rock substrates can indicate biological processing and accumulation. In contrast, atmospherically-deposited cations, derived from dust and marine aerosols[2], will be isotopically similar to or heavier than common rocks particularly in areas where marine aerosols with characteristically heavy Ca[8], Sr[9] and Ba[10] dominate.

2. Site description and methods

The Kohala soil climosequence lies on the western limb of Kohala Mountain, the oldest of five shield volcanoes on Hawaii, and is developed on 0.23 to 0.12 Ma Hawi Volcanic Series (HVS) alkalic cap lavas and ash that range in composition from hawaiite to trachyte[11]. The main climate variable is median annual precipitation (MAP), which varies from ~160mm near the coast to >4000mm near the mountain crest at 4700m elevation. Details of geomorphology, climate, vegetation, water balance and soil sampling procedures and locations are given elsewhere[5]. Briefly, with increasing elevation and MAP a sequence of soil process domains separated by pedogenic thresholds has been identified[12]. For MAP<700mm, there has been only minor cation loss and soil formation can be influenced by pedogenic carbonate deposition and is limited by wind erosion. For MAP from ~700mm to 2100mm, cation loss due to leaching is greater but evidence for biolifting of rock-derived nutrients is best observed. For MAP>2100mm, cations have been largely leached, aluminum mobility and iron redox processes predominate and soil fertility is low. The distribution of $^{87}Sr/^{86}Sr$ reveals dominance of HVS rock-derived Sr in the cation exchange and bulk soil pools up to the 2100mm MAP threshold, and seawater- and Asian dust-derived Sr in those pools at wetter sites[4].

For this study, our goal was to interpret the isotope composition of the soil cation exchange pool which we take to represent an integrated record of pedogenic processes (e.g. chemical weathering, secondary mineral formation, atmospheric deposition, biologic cycling, hydrologic transport)[13]. Soils from previously well-characterized depth profiles at three sites showing evidence for P biolifting were selected for isotope analysis: site E (elevation: 674m; MAP: 570mm), site I (1090m; 1260mm) and site J (1134m; 1380mm). In addition a profile from higher elevation, site L (1254m; 3000mm), was selected for comparison. The <2mm fractions of the soils were exchanged using 0.1M ammonium acetate to obtain the labile fraction. In addition eight lava and tephra samples spanning the range of HVS compositions were analyzed in order to identify potential isotope variability in the soil parent materials. Finally, an Ohi'a tree seedling collected from a recent lava flow at the southeast corner of Hawaii was separated into root, stem and foliage for analysis in order to assess the ability of plants to extract light Ca, Sr and Ba from fresh rock substrate. Element concentrations in exchange and rock and tree tissue digest solutions were measured using inductively coupled plasma mass spectrometry. Calcium, Sr and Ba isotope ratios were determined using "double spike" thermal ionization mass spectrometry. Results are expressed in "delta notation", the permil difference of the measured ratio of a sample compared to that of NIST 915A for Ca, NIST 987 for Sr, and NIST 3104a for Ba.

3. Linking the alkaline earth elements and their isotopes to biolifting

Net gain or loss of an element in soil systems is commonly assessed by considering tau (τ) values defined as:

$$\tau = ((C_{ei,w}/C_{ie,w}) / (C_{ei,p}/C_{ie,p})) - 1 \quad (1)$$

where C_{ei} is the concentration of the element of interest, C_{ie} is the concentration of an immobile element, w represents weathered horizons and p represents parent material[14]. We used niobium (Nb) as the immobile element

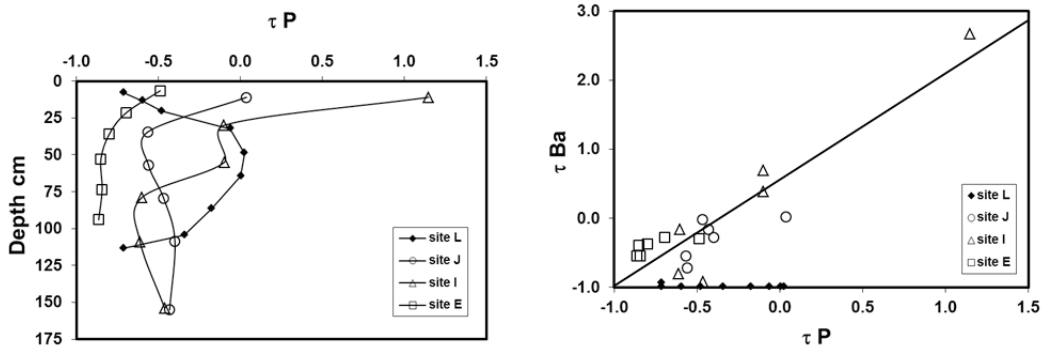

Fig.1. (a) τP vs. depth for sites along Kohala climosequence. Open symbols show sites having evidence for P biolifting, closed symbols show a higher MAP site for reference. (b) plot of τBa vs τP for the same sites with correlation regression line for sites having evidence of P biolifting. Positive τ values represent a net gain of the element, negative values represent a net loss of the element relative to the parent material (τ=0).

for the calculation due to its demonstrated immobility in Hawaiian soils[15]. The parent material composition for each soil sample was constrained by relating the ratio of titanium (Ti) to Nb (Ti/Nb) of the soil sample to HVS rocks having the same Ti/Nb ratio and using corresponding ratios of P/Nb, Ca/Nb, Sr/Nb and Ba/Nb. In Figure 1a we plot resulting tau values for P (τP) for the <2mm soil fractions for soil profiles from four sites along the climosequence, three of which (sites E, I, J) show evidence for P biolifting (i.e. surface soils have elevated τP relative to soils at depth) while the profile from higher-MAP site L shows no enrichment of P at the surface. We note that at site E some surface soil has likely been removed due to wind erosion and that τP in the removed soil was likely greater than that in the current surface soil. In Figure 1b we compare tau values for Ba (τBa) with τP for these sites, and highlight the correlation between these two parameters (r^2=0.82, n=18) for the sites having evidence for biolifting. Similar positive relationships with τP are observed for τCa and τSr at the sites having evidence for P biolifting.

Isotope data for the exchangeable fraction of the soils are plotted in Figure 2, along with several pertinent system components that have bearing on interpretation of isotope variations observed in the exchange pool. The paired vertical bands in each figure show the range of isotope composition of the HVS lavas and tephra measured in samples for this study, helping to constrain the composition of soil parent materials. Such isotope variability of Ca, Sr and Ba in fresh igneous rocks was unanticipated but points to igneous processes such as of plagioclase feldspar fractionation as the primary control. The horizontal line along the isotope axis in each plot shows the range of Ohi'a tree tissues (roots, stem, foliage) of the seedling plucked from a recent lava flow elsewhere on the Big Island. These tree tissue data demonstrate that plants selectively take up the lighter isotopes of Ca, Sr and Ba even from fresh lava substrates. Finally, values for the isotope composition of seawater are shown to help constrain the composition of Ca[8], Sr[9] and Ba[10] likely to be derived from aerosols in this near-marine setting.

At sites having evidence for biolifting of P (sites E, I, J), the shallowest samples have the lightest compositions of exchangeable Ca, Sr and Ba all of which lie to the light side of the range of compositions for HVS soil parent materials. For each isotope system, these light isotope compositions project toward the range for the Ohi'a tissues which we propose are representative of plants growing on fresh lava surfaces. Taken together these data suggest that during pedogenesis at these sites, plants have selectively taken up light Ca, Sr and Ba from the HVS parent materials and concentrated that light fraction at the surface consistent with nutrient (and proxy) biolifting. We note that at site E wind erosion may have removed an even lighter biolifted pool than is evident in present-day surface soils.

With increasing depth, exchangeable Ca, Sr and Ba become heavier although the patterns of increasing heaviness differ between the systems. The Ba isotope profiles provide the clearest evidence for a connection to biolifting, as exchangeable Ba for all samples below the shallowest sample at each site is heavier than Ba in the HVS parent materials. A straightforward interpretation of the Ba patterns is that Ba having the isotope composition of the HVS parent materials was mobilized during weathering and separated into two fractions, a light fraction biolifted by plants and a heavy fraction that remained on exchange sites. The increase in heaviness with depth for the Ca and Sr isotope patterns is more gradual than for Ba, which we infer to have resulted from a greater "leakiness" of Ca and Sr from the shallow soils during infiltration of precipitation. We suggest that light biolifted Ca

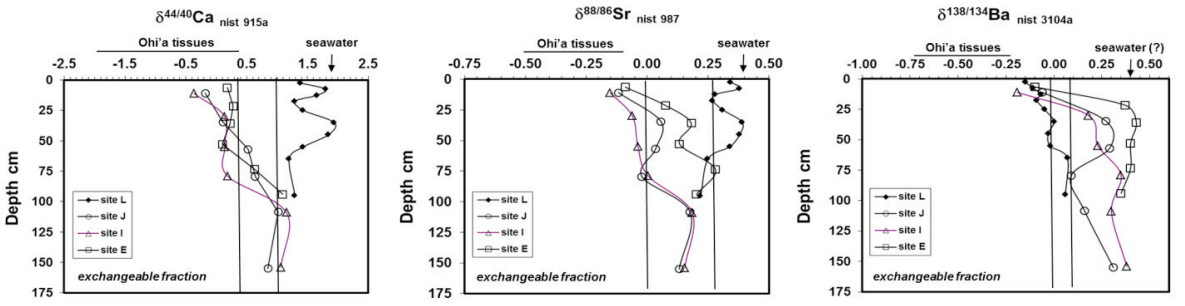

Fig. 2. Isotope compositions of Ca, Sr and Ba measured for this study. Depth patterns for each site are for the exchangeable fraction of the soils. Vertical bands in each plot show the range of composition in HVS lavas and tephra. Horizontal line along the isotope axis in each plot gives the range of composition observed in Ohi'a tissues (root, stem, foliage). References for values of Ca, Sr and Ba in seawater are given in the text.

and Sr leached from shallow soils continually overprint deeper exchange sites while light biolifted Ba is efficiently retained by the shallow soils consistent with previously recognized greater sorption potential of Ba relative to that of Ca and Sr[16]. The impact of progressive leaching of Ca and Sr from, but retention of Ba by shallow soils is evident in the isotope profiles for exchangeable fractions at the high MAP site L. At this site the isotope compositions of exchangeable Ca and Sr are shifted toward seawater values and reasonably reflect a mixture of Ca and Sr derived from dust and marine aerosols consistent with interpretations based on $^{87}Sr/^{86}Sr$ of the labile fraction of soils from this site[4]. In contrast, the Ba isotope profile has the same general form as those from lower elevation sites and clearly has retained a record of biolifted Ba in spite of near total leaching of most cations from these wet soils[5].

Our results suggest that Ca, Sr and Ba stable isotopes together constitute a useful diagnostic tool for distinguishing biolifting vs. deposition from atmospheric sources to explain distributions of inorganic rock-derived nutrients in soils and may provide an interpretable gradient of response to changing climate. Future application of this approach may be particularly useful in the study of eroded or disturbed surfaces and paleosols.

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